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⑬ CANADIAN PATENT

⑭ PROCESS FOR PYROLYTICALLY DEGRADING BARK.

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No. OF CLAIMS 6

932686

The present invention concerns the production of valuable products through the pyrolytic degradation of bark.

The bark of trees, such as Douglas fir and pine, comprises a significant by-product of the wood products industry. Such bark contains a number of complex chemical substances which, through pyrolysis, yield organic materials of commercial utility. The production of such organic materials, however, is only practical if yields are in sufficient quantity, and the cost of producing such yields is low enough,
10 as to be justified economically.

A general object of this invention is to provide an improved process for pyrolytically degrading bark which results in the production of significantly larger yields of a useful organic material, namely, a tar-oil product, than previously possible. As used herein, the phrase "tar-oil" product refers to that portion of the volatile products given off on the pyrolytic degrading of bark which is condensable under atmospheric conditions.

More specifically, this invention is based on the
20 discovery that maximum yields of a tar-oil product are possible if the bark is quickly brought to pyrolysis temperature, and volatile product produced by the pyrolysis is handled in such a way as to inhibit further pyrolysis to produce a noncondensable material.

Thus, a more specific object of the invention is to provide a process for the pyrolytic degradation of bark, wherein a fluid bed reactor is employed, which enables the bark quickly to be brought to pyrolysis temperature as part of a fluidized bed, and wherein the retention time within the reactor of volatile product produced during the pyrolysis is
30 maintained at a minimum. The retention time of the solid product which results from the pyrolysis, i.e., char, while not



of great length, is considerably longer than the retention time of the volatile product. The retention time selected for the solid product is one which permits maximum pyrolytic conversion of the bark to a tar-oil product under the reaction conditions being maintained.

As already indicated, the bark is brought to pyrolysis temperature as a part of a fluidized bed, i.e., a bed comprising a mass of bark particles existing as a turbulent mass with particles suspended by a fluidizing gas traveling
10 up through the mass. Because of the suspended state of the particles, the mass has many of the properties of a fluid. Some of the gas producing fluidizing of the bed comprises the volatile product driven off from the bark particles as the result of pyrolysis. Additional fluidizing gas is introduced to the base of the fluid bed reactor and directed to flow upwardly through the bed of bark particles. To permit optimum recovery of volatile pyrolysis product, it is desired to minimize the dilution of the volatile pyrolysis product by the fluidizing gas introduced to the base of the reactor. Toward
20 this end, the fluidizing gas introduced to the reactor is introduced primarily at the start of fluidizing the bed, and the gas subsequently introduced preferably is only that which is necessary to maintain the bed in proper fluidized form.

With the introduction of fluidizing gas controlled in the manner set forth above, it is not practicable to control the temperature of the fluidized bed by relying on a heat transfer between the fluidizing gas and the particles in the bed fluidized. As a consequence, this invention further contemplates, as a specific object, a process wherein temperature
30 control of the fluidized bed is effected by a heat exchange taking place between the bed and heat transfer surfaces in the bed, which surfaces are controlled as to temperature to

produce the results desired. Further explaining, and assuming that a temperature of 1,000° F. is desired in the fluidized bed, and the heat must be introduced into the bed for it to be maintained at this temperature level, such heat may be introduced by circulating a hot gas through tubes or other heat exchange surfaces provided in the region of the bed, with heat transferring from these surfaces to the particles making up the bed.

The invention, and various other objects, features, and advantages of such, will become more fully apparent from
10 a reading of the following description, which is to be taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a flow sheet illustrating a preferred manner of carrying out the invention; and

FIGURE 2 illustrates a fluid bed reactor such as is used in carrying out the invention.

In practicing the invention, bark, such as the bark of Douglas fir, pine, hemlock, etc., may be first processed to remove metal objects, stones, dirt, etc. The bark is then
20 dried, and reduced to particle form, whence it is ready to be subjected to pyrolysis.

In the pyrolysis of the bark, the particulate bark material is fed continuously into a fluidizing zone of a fluid bed reactor. This zone is maintained at a temperature within a critical temperature range, noted to be high enough to promote the desired pyrolytic conversion of the bark to a tar-oil product, and not so high as to produce material degradation by further pyrolytic action of this product into lower molecular weight materials, such as noncondensable gases. The bark
30 particles are maintained in a fluidized state, by introducing a fluidizing gas from a source outside the reactor, which moves up through the bed together with volatile product produced

932686

by the pyrolysis. The volatile product of the pyrolysis is removed almost immediately, with a retention time in the reactor of less than ten seconds being deemed required to obtain the yields desired, and a retention time of less than seven seconds being preferred. The volatile product from the pyrolysis is directed to a condensor, where the condensables are reduced to liquid form. The noncondensable portion of such volatile product (which contains a significant amount of combustible gas) may be used in the firing of the dryer, or in
10 other parts of the general process, as a source of heat. The liquid condensates may then be further processed, in order to separate such material into fractions of different boiling points.

In carrying out the instant invention, while it is critical that the retention time of the volatile product of the pyrolysis be less than about ten seconds, the retention time of the solid product in the reactor should be substantially greater. A retention time of two minutes is considered the minimum, and a retention time of at least three minutes is preferred. It is only with a retention time as indicated that
20 desired yields in volatile product are obtained.

For the purpose of better understanding this part of the invention, a typical fluid bed reactor will be described, and reference is now made to FIGURE 2.

The fluid bed reactor illustrated in FIGURE 1 comprises a reactor shell 10 including a substantially cylindrical bottom wall section 10a, and an upper section 10b of slightly larger diameter joining with this bottom section. A perforated distributor tray 12 extends across the bottom section, and this tray
30 defines the base of the fluidizing zone in the reactor. Wall 10a bounds the periphery of this zone.

Comminuted bark to be processed in the reactor enters

932686

through a feed pipe 14, with valve 16 providing a means for controlling the feed rate of the bark. The bottom of the feed pipe opens to the interior of the reactor shell to provide adequate distribution of bark to the fluidizing zone within the reactor.

Solid product (char) produced in the pyrolysis leaves the reactor through conduit 18. Solid product moves into the conduit by spilling over from the top of the fluidizing zone. Conduit 18 is provided with a valve 20. With valve 20 opened, 10 the retention time of solid product in the reactor is controlled entirely by control of the feed rate of bark through feed pipe 14. The average retention time of solid product within the reactor is calculated by dividing the amount of solid product which is containable within the fluidizing zone as a fluidizing bed by the feed rate of comminuted bark into the reactor through the feed pipe. With partial closing of valve 20, the size of the fluidized bed within the reactor may be increased which has the effect of also increasing the retention time of the solid product.

20 Shown at 26 are tubes which project into the fluidizing zone of the reactor. These are utilizable in controlling the temperature of the bed during the pyrolysis. Thus, if heat is to be supplied to the reaction zone, hot gas may be circulated through these pipes, with the heat exchange taking place between the hot gas and the material in the bed through the pipe surface which constitute heat exchange surfaces.

Shown within the reactor is a cyclone separator 30. Such communicates adjacent its top with the interior of the reactor, through a duct 32. Solid fines collecting in the 30 cyclone separator drop down in the separator to collect in a pipe 34. These fines are withdrawable periodically by opening valve 36.

Volatile product produced by the pyrolysis leaves the reactor by entering the cyclone separator through duct 32, and thence passing upwardly through conduit 38 which leads from the top of the separator and outside the retort. Such volatile product is essentially free of solid material and comprises condensables, which condense to produce water and a tar-oil product, and noncondensables, comprising carbon dioxide, carbon monoxide, methane and other gaseous products. This noncondensable volatile product may be utilized as a
10 fuel in carrying out other parts of the process.

During the pyrolysis of the bark, volatile product is given off which is utilized in fluidizing the bed in the reactor. Additional gas to fluidize the bed is introduced into the reactor through conduit 40 at the base of the reactor. The gas utilized may be steam, which is a condensable material and thus removed with condensation of the material leaving the reactor. Another gas that may be employed is the noncondensable gas produced by the pyrolysis, which, as already indicated, includes appreciable amounts of carbon monoxide and carbon
20 dioxide.

Referring now to FIGURE 2, which is a flow diagram illustrating how bark may be processed according to the invention, shown at 50 is a bark storage pile from which bark is conveyed on conveyor 52 past a magnet 54 where tramp iron is removed magnetically. From thence, the bark travels into a water sluice 56, with heavy articles such as rock and stones being removed by falling to the bottom of the sluice. Bark flowing with the water through the sluice is thence tumble washed in a washer 58 where silt and mud are removed. The bark
30 after being drained of excess water is conveyed to a roll press 59 where, through a squeeze action, there is a reduction in moisture content, and initial breaking up of bark chunks occurs.

932686

Bark leaving the roll press passes on a conveyor 62 to a dryer 64, where the bark is dried to a moisture content of less than about 20 percent moisture (percent by weight water based on the dry weight of the bark). Preferably, the bark is dried to an oven dry state. In the dryer, the combustible non-condensable gas materials produced in the pyrolysis reaction may be utilized to provide the fuel requirements of the dryer.

Dry bark from the dryer is comminuted by directing the bark on a conveyor 66 to a grinder 68 where the bark is reduced to proper particle size to permit the formation of
10 fluidized bed. Ordinarily, it is contemplated that the bark is ground to a particle size permitting it to pass through at least about a quarter-inch screen. On leaving the grinder, the bark is screened at 69, and transported to a feed bin 70 where such is stored prior to being introduced to the fluid bed reactor, shown generally at 71.

The fluid bed reactor has already been described in some detail in connection with FIGURE 2. Solid product (carbon or char) from the reactor, is collected in carbon cooler 72
20 whence it is conveyed to a carbon bin 74.

The volatile product from the pyrolysis reaction passes through conduit 75 to a condensor 76 where the temperature of the volatile product is reduced from approximately the temperature of the fluid bed reactor to a temperature near room temperature, i.e., 100° to 200° F. The noncondensable product from the condensor, which typically may comprise from 60 to 64 percent carbon monoxide, 13 to 19 percent methane, and 17 to 26 percent carbon dioxide, travels through a conduit 78 to a gas holder 80, where such is stored prior to being used for fuel
30 purposes. The condensable material from the condensor (the tar-oil product and water), travels to a tank 82. From thence, the material may be further processed to recover specific

organic compounds from the condensables.

In the figure, a still is shown at 86 where the condensable material from the condensor may be initially processed. In the still, so-called light oils, i.e., organic compounds boiling lower than phenol, are separated together with water from organic compounds having a boiling point equal to or greater than phenol. The water and light oils leave the still at the top and travel through conduit 88 to additional distillation equipment 89 where there may be final recovery of the organic material in this fraction. The heavier boiling material leaves the still at the bottom, and travels through conduit 90 to additional distillation equipment where there may be further separation into portions of different boiling points.

The following examples serve to illustrate the invention, as practiced with certain types of tree barks.

Example 1

Ground carbon passing through a twenty-mesh screen was placed in a fluid bed reactor of the type illustrated in FIGURE 2. Steam was introduced into tubes 26, to raise the temperature of this carbon to a temperature of 800° F. Fluidizing gas, i.e., steam, at approximately the bed temperature of 900° F., and at a pressure of 15 psig, was introduced into the reactor through conduit 40. The steam produced a fluidized bed of the carbon having a density of 1.52 pounds per cubic foot, which filled up the fluidizing zone within the reactor.

Old growth Douglas fir bark, processed as with the equipment shown in FIGURE 1 to have a particle size passing through a twenty-mesh screen, and nearly at oven dry moisture conditions, was then introduced continuously into the fluid bed reactor through conduit 14. The solid product of pyrolysis,

i.e., char, was removed continuously through conduit 18, as such spilled over into the conduit.

During pyrolysis, sufficient steam, as fluidizing gas, was introduced into the reactor to maintain the particles within the reactor as a fluidized bed having the density earlier indicated. As pyrolysis proceeded, the amount of steam needed to maintain the bed properly fluidized dropped by about 70 percent.

10 Average retention time of solid product within the reactor was determined by dividing the weight of bark that the fluidizing zone of the reactor could hold with such in the form of a fluidized bed, with the feed rate introduced of bark into the fluidizing zone. The average retention time of solid product in the reactor was determined to be 3.73 minutes. Knowing the volume of the reactor occupied by volatile products of reaction, the total flow rate of gas out from the reactor, and the flow rate of fluidizing gas into the reactor, the average retention time of volatile product within the reactor was determined, and found to be 3.70 seconds.

20 Using the fluidizing bed temperature of 800° F., and with the residence times indicated for the solid and volatile products of the reaction, the following yields were obtained (expressed as percent by weight of the oven dried bark processed): tar-oil 32.41; char 33.51; water 20.17; noncondensables or gas 15.90.

In other runs, old growth Douglas fir bark was processed as in Example 1, using different bed temperatures for the fluidized bed. The yields obtained in these different runs are indicated in the following table:

932686

Table I

	<u>Bed Temperature degrees F.</u>	<u>Yield as percent by weight of oven dry bark</u>			
		<u>Tar-Oil</u>	<u>Char</u>	<u>Water</u>	<u>Gas</u>
Example 2	700	23.06	43.65	29.12	4.17
Example 3	900	31.83	27.33	18.37	22.47
Example 4	1100	23.51	22.04	14.98	39.47
Example 5	1500	4.61	11.26	16.09	68.04
Example 6	500	5.27	82.58	10.01	2.14

10 In other runs, other types of bark were processed, using various bed temperatures, as indicated by the following summarizing table:

Table II

	<u>Bed Temperature degrees F.</u>	<u>Yield as percent by weight of oven dry bark</u>			
		<u>Tar-Oil</u>	<u>Char</u>	<u>Water</u>	<u>Gas</u>
Example 7 (Second growth Douglas fir)	900	26.76	35.52	22.10	15.62
Example 8 (Second growth Douglas fir)	1000	28.32	31.65	23.18	16.85
Example 9 (Second growth Douglas fir)	1100	25.59	29.70	16.36	28.35
Example 10 (Hemlock)	1100	27.18	30.55	18.03	24.24

Example 2

30 In another run, old growth Douglas fir bark was processed, as in Example 3, utilizing a bed temperature of 900° F., but with carbon dioxide introduced into the fluid bed reactor (at the bed temperature utilized) as the fluidizing gas, instead of steam. The yield produced from bark so processed was as follows: Tar-oil 34.12; char 33.73; water 24.27; gas 7.88.

932686

As partially demonstrated by Examples 5 and 6, to obtain maximum yields the temperature for the fluidized bed during the pyrolysis reactor preferably should be within the range of 700 to 1200° F. The temperature employed in the fluidized bed depends to some extent on the type of bark being processed, with it being observed that old growth Douglas fir is best processed at a temperature of around 900° F., second growth Douglas fir and southern pine at temperatures between 900° F. and 1000° F. and hemlock at a temperature slightly
10 exceeding 1000. When too high a temperature is used, apparently through pyrolysis the volatile product obtained is excessively degraded to a noncondensable state, and thus not recoverable as a tar-oil product. With too low a temperature used, insufficient pyrolysis takes place to give proper yields.

According to the invention, it is extremely important that the retention time of the volatile product in the pyrolysis reaction, i.e., the gas phase, be less than ten seconds and preferably under seven seconds, if maximum yield of tar-oil product is to be realized. For instance, as demonstrated in
20 Example 9, a tar-oil yield of 25.59 percent was obtained with a gas retention time of 3.70 seconds. Increasing this retention time to 5.22 seconds (by lowering of the flow rate of fluidizing gas through the reactor) had the effect of reducing the tar-oil yield to 19.06 percent. With a retention time above 10 seconds, a very serious reduction in tar-oil yield will be experienced. As a practical matter, retention times of less than about two seconds are difficult to obtain, due to the high velocity of gas flow that would be required through the reactor to obtain this very low retention time.

30 The solids preferably are retained within the reactor for a retention time ranging from two to about six minutes. A retention time exceeding the range indicated does not appear to

affect the yield of tar-oil obtained. However, the yield of solid char or charcoal is affected, with a long retention time apparently having the effect of causing loss of carbon with the production of noncondensables such as carbon dioxide and carbon monoxide. Without a retention time of at least about two minutes, there is insufficient pyrolytic action to obtain the desired yield.

10 In the examples above set forth, external heat was applied to the fluid bed reactor, through tubes 26 at start-up and to a limited degree during the pyrolytic reaction, to maintain the bed temperature at the level desired. This permitted the fluidizing gas to be introduced at the exact temperature desired in the fluidized bed, and permitted temperature control without relying upon heat contributed as sensible heat in the fluidizing gas. As a consequence, minimum dilution of the volatile product obtained by the pyrolysis results.

20 The tar-oil products obtained in the various runs set forth above were processed, to determine the fraction of such products comprising organic compounds with boiling points lower than that of phenol, considered the "light oils", and to determine the fraction of such tar-oil products, having boiling points equaling that of phenol and ranging upwardly to the boiling point of dimethyl catechol (the latter fraction being referred to as the mixed phenolic fraction). The light oil fraction contains such compounds as organic acids, aldehydes, ketones, ethers and alcohols. The mixed phenolic fraction contains such compounds as phenol, cresols, xylenols, guaiacol, alkyl phenols, and certain dehydric phenols such as the catechols. The fraction having a boiling point exceeding that of dimethyl
30 catechol was classed as a heavy oil fraction, and is made up of complex polyphenolic compounds, a significant portion of such

932686

being wax esters of ferulic acid and lignoceryl alcohol, and/or similar type esters. The following table summarizes the results obtained from such processing.

The various phenolic compounds obtained from the mixed phenolic cut, i.e., the compounds with a boiling point ranging from that of phenol to that of dimethyl catechol, have utility in the usual applications requiring phenolic compounds. For example, they may be used in phenolic resins, plasticizers, pesticides, and as chemical intermediates.

With respect to what are referred to herein as the heavy oils of the tar-oil product, such have utility in the preparation of plywood adhesives, molding resins, extenders for epoxy resins, compounding aids for rubber, plasticizers, blending aids for high density polyethylenes, resin adhesive for Fiberglas products, etc. To illustrate just one of such uses, a plywood adhesive was prepared with 30 percent of the phenol in a phenol-formaldehyde resin replaced with the heavy oil fraction mentioned. The adhesive prepared was comparable to commercial resins produced entirely from phenol.

20

The char or carbon product which is obtained by the pyrolysis is produced in approximately the particle size of the bark product from which the char is prepared. Such may be briquetted in a conventional manner, to produce charcoal briquets usable for fuel purposes. Alternatively, the carbon may be activated to produce an activated carbon usable in such fields as municipal water purification, sugar processing, dry cleaning, gas absorption, etc.

While having described particular embodiments of the invention, it is appreciated that changes and variations will
30 occur to those skilled in the art.

TABLE III

Composition of Tar-Oil Product (% by weight)

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Light Oils	10.07	9.12	8.19	10.61	8.71	6.81	8.33	8.59	9.16
Phenol and guaiacol	1.61	1.74	1.37	1.75	0.89	0.86	1.82	3.04	1.52
O-cresol and creosole	0.89	0.45	0.52	1.30	0.21	0.59	1.39	0.96	1.39
p-cresol and m-cresol	1.50	1.44	0.82	1.34	0.61	0.74	1.92	2.63	1.44
Xylenols and subs. phenols	2.96	2.19	5.74	3.12	1.84	1.80	5.24	1.64	5.38
Catechol	2.35	2.10	2.93	3.51	3.52	3.13	4.15	3.58	3.49
3-me-catechol	1.10	1.17	1.06	0.89	0.89	0.86	0.94	0.50	1.80
4-me-catechol	2.74	2.84	3.25	3.75	3.13	3.49	3.72	2.31	3.04
di me-catechol	1.28	0.58	2.52	1.98	1.23	1.31	1.31	1.34	2.51
Heavy Oils	75.50	78.37	73.20	71.75	78.97	80.41	71.18	75.41	70.27

Mixed
Phenolics

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for pyrolytically degrading bark comprising

reducing the bark to particle form suitable for the formation of a fluidized bed,

introducing such bark to the fluidizing zone of a fluid bed reactor and with such zone at a temperature of from 850° to 1100° F. producing a fluidized bed from such bark,

through pyrolysis degrading the bark in such fluidized bed to produce a volatile product and a solid char product,

after an average retention time in the reactor of no more than about ten seconds removing the volatile product from the reactor, and

after an average retention time in the reactor of no less than two minutes removing the solid char product from the reactor.

2. The method of claim 1, wherein the bark prior to introduction to the fluidizing zone is dried to a moisture content of 20 percent or less.

3. The method of claim 1, which further comprises the step of heat exchange with bark in said fluidizing zone through heat transfer surfaces disposed in said zone, to maintain the temperature in said zone between 700° and 1200° F.

4. The method of claim 1, wherein the volatile product from the bark is removed after an average retention time ranging from two to seven seconds, and the solid product is removed after an average retention time ranging from two to six minutes.

5. The method of claim 1, wherein the bark prior to being introduced to the fluidizing zone is dried to a moisture content of 20 percent or less, and wherein heat exchange takes place with bark in said fluidizing bed zone through heat transfer surfaces disposed in said zone, to maintain the temperature in said zone between 700° and 1200° F.

6. The method of claim 1, wherein the fluidizing zone is bounded by a peripheral upright wall, the bark is fed continuously into said zone, and solid pyrolysis product is removed continuously as such spills over said wall.



932686
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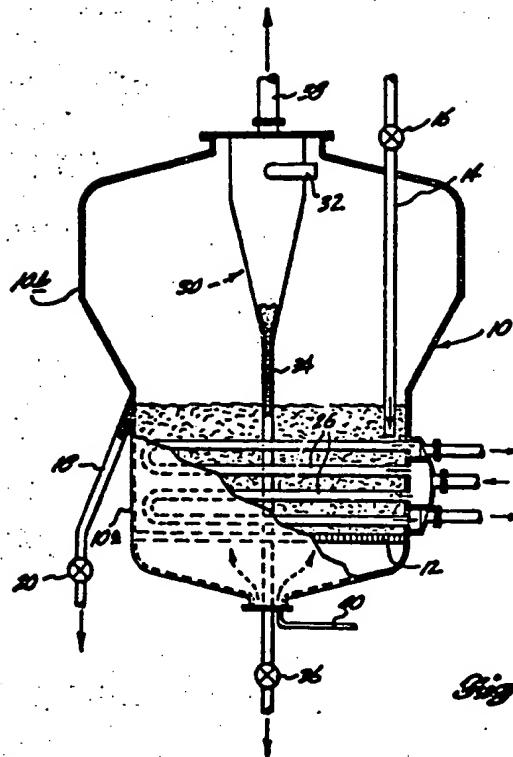
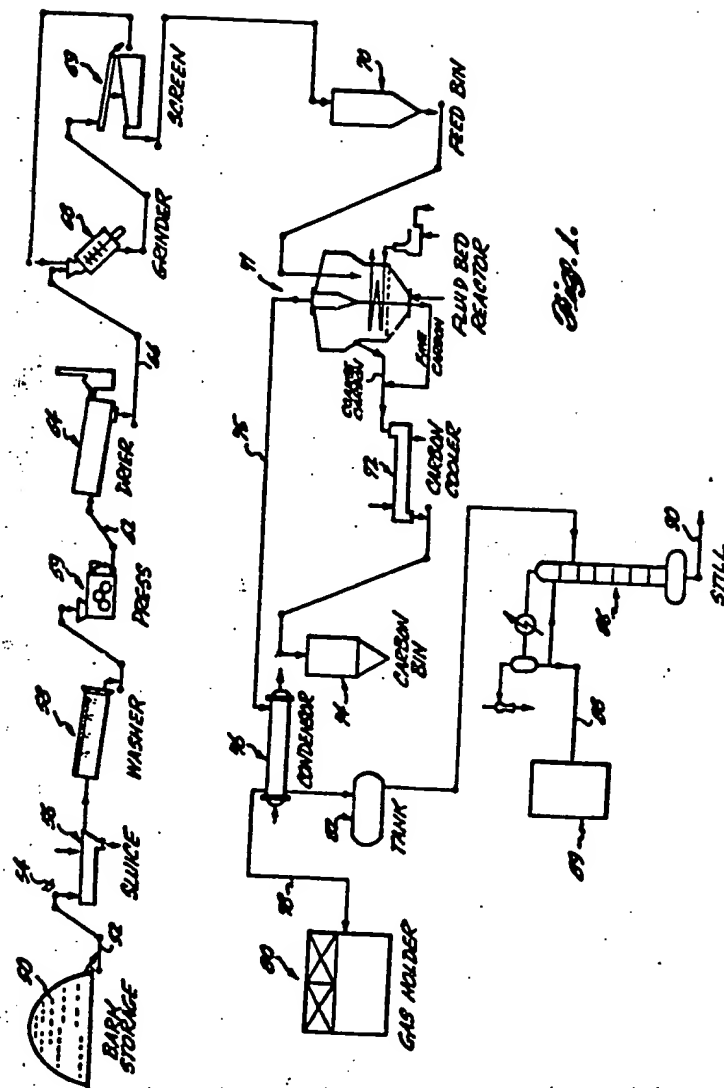


Fig. 2.

932686
2-1



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